

# Perfluorinated polyethers for the immobilisation of homogeneous nickel catalysts

W. Keim<sup>\*</sup>, M. Vogt, P. Wasserscheid, B. Drießen-Hölscher

*Institut für Technische Chemie und Petrochemie der RWTH Aachen, Worringer Weg 1, 52074 Aachen, Germany*

Received 30 April 1998; accepted 28 May 1998

## Abstract

The perfluorinated polyether Hostinert 216<sup>®</sup> is used as catalyst phase in a biphasic oligomerisation of ethene using a nickel catalyst with adapted designed ligand. The synthesis of the catalyst from hexafluoropropenoxide and Ni(COD)<sub>2</sub> is described. The catalytic results show the usefulness of fluorinated solvents for the immobilisation of homogeneous catalysts. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Fluorous biphasic systems; Oligomerisation; Immobilisation; Catalysis

## 1. Introduction

Liquid–liquid biphasic systems have attracted much attention during the last years for the immobilisation of homogeneous catalysts. This principle was realised first industrially in the SHOP (Shell higher olefins process) [1,2] followed by the Ruhrchemie/Rhone-Poulenc process [3,4]. While in the former case the Ni catalyst is dissolved in 1,4-butanediol to form a second layer with the  $\alpha$ -olefin produced from ethene, water is used in the latter case as catalyst phase.

Several other catalyst systems have been investigated since then in aqueous biphasic systems and some of them have been applied industrially as well [5,6]. Unfortunately, aqueous

biphasic processes cannot be carried out if one of the system's components undergoes undesired side reactions with water. Another potential limitation is the low solubility of some organic substrates in water.

Fluorocarbons are characterised by their non-polar nature and low intermolecular forces. Their miscibility with water and with most common organic solvents such as toluene, ethanol, tetrahydrofuran and acetone is low and those mixtures form biphasic systems under appropriate conditions.

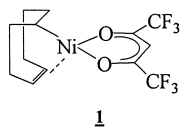
In 1994 Horváth and Rábai published in Science their work on the Rh-catalysed hydroformylation of higher olefins (1-octene and 1-decene) in perfluorinated solvents. The catalyst was prepared in situ from [Rh(CO)<sub>2</sub>(acac)] (acac = acetylacetonate) and P[CH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>5</sub>CF<sub>3</sub>]<sub>3</sub> (P/Rh = 40) to ensure high solubility in the fluorous medium [7]. Following this

<sup>\*</sup> Corresponding author. Fax: +49–241–8888177

report the same methodology has been employed for a number of other transition metal catalysed reactions: besides the hydroboration in  $\text{CF}_3\text{C}_6\text{F}_{11}$  with a similar modified rhodium catalyst [8] the applications published so far mostly deal with oxidation reactions which benefit from the high solubility of  $\text{O}_2$  in perfluorinated solvents. Pozzi et al. [9] reported on epoxidation of cyclic and aliphatic olefins with Co-complexes containing modified tetraalkylporphyrine ligands. Klement et al. [10] described the oxidation of aldehydes, sulfides and olefins with perfluorinated Ni and Ru-acac catalysts. Modified 1,4,7-triazacyclononan ligands were used as ligand in Mn and Co catalysts by Vincent et al. [11]. The common principle of all these publications is that the transition metal is modified with a long perfluorinated alkyl group ('ponytail') which renders these substances soluble in a perfluorocarbon phase allowing the facile separation of the catalyst, after reaction.

We wish to report here that the use of perfluorinated substances as solvents for catalyst immobilisation as well as the concept of tailoring adapted fluorinated ligands to provide high catalyst solubility was investigated many years earlier (1991) by us in the PhD thesis of Vogt [12] and represents the first work on the use of biphasic systems with fluorinated solvents [13,14].

Our aim at this time is the development of alternative solvent systems for the biphasic oligomerisation of olefins with the Ni catalyst **1**.



To our knowledge **1** is the best known catalyst system for the homogeneous, linear dimerisation of higher ( $> \text{C}_2$ ) olefins in organic solvents [15,16]. Using **1** in organic solvents, 1-butene could be dimerised with a TOF of  $500 \text{ h}^{-1}$  to a mixture of octenes wherein 75% were

Table 1

Catalytic results of **1** for the dimerisation of different olefins in toluene at  $90^\circ\text{C}$  [15]

Olefin	TOF (mol/mol $\text{h}^{-1}$ )	Selectivity to dimers (%)	Linearity of dimers (%)
Ethene	8200	20	100
Propene	800	60	75
1-Butene	500	85	75
1-Hexene	300	90	60
1-Octene	50	100	82

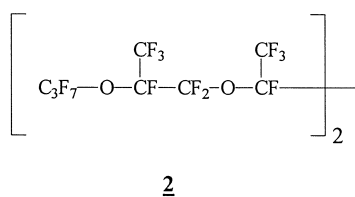
linear. The high linearity of the dimers obtained make them an ideal feedstock for plasticizers with better thermal efficiency. Table 1 shows the results of this catalyst system with different olefinic feedstocks.

Although these results regarding linearity obtained are very interesting, the high costs of the hexafluoroacetylacetonate ligand, the quite low activity of the catalyst especially for higher olefins and the difficulty to recycle the catalyst has prevented greater industrial interest until now.

To overcome the problems listed, much work in our group has been directed towards the heterogenisation of the catalyst **1**: Gruppe [17] tried to anchor **1** on polymer surfaces, while Mehlhorn et al. [18] investigated the introduction of the above mentioned Ni catalyst into zeolites. These strategies, however, resulted in strong catalyst leaching and much lower activity. As an alternative possibility for the immobilisation of **1** the reaction in a biphasic mode has been investigated, but all of the common polar solvents (water, butanediol, etc.) have shown fast deactivation of the catalyst.

## 2. Experimental

At this point we developed the concept of using the perfluorinated ether Hostinert 216<sup>®</sup> **2** as catalyst solvent for **1**. We wanted to benefit from its low solubility for the olefinic product. Our aim was to realise an easy catalyst recovery and recycling approach.



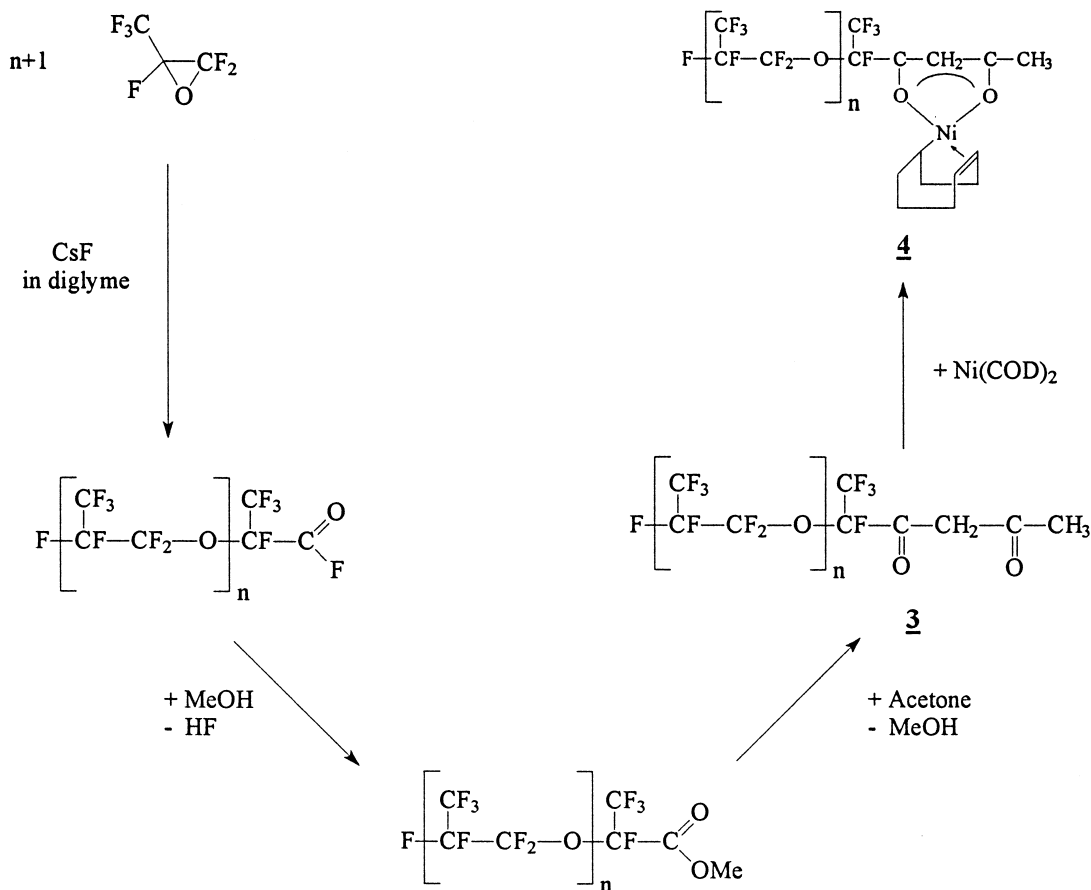
It was possible to dissolve **1** in Hostinert 216<sup>®</sup>, but an extraction of the catalyst into the upper layer of oligomers produced was observed during the reaction.

It has been known for centuries that ‘similia similibus solvuntur’ or ‘like dissolves like’. Keeping this in mind we started to design a ligand system very similar to Hostinert 216<sup>®</sup> using the same building blocks as for Hostinert

216<sup>®</sup> thus building a fluorinated ligand tail as shown in Scheme 1 for the synthesis of **4**.

According to this principle we used hexafluoropropyleneoxide (HFPO) for the tail synthesis. It is known that HFPO reacts in the presence of CsF in suitable solvents to form oligomers [19]. These oligomers can be separated by a distillation procedure and HFPO trimers (b.p. 113–115°C), tetramers (b.p. 158–161°C), and pentamers (200–203°C) are obtained. The product can be characterised easily by IR spectroscopy.

To functionalise these oligomers to the required 1,3-diketo compound, we transformed the acidic fluoride compound first into the corresponding methylester by simple addition of methanol. It is noteworthy that the HFPO<sub>3</sub>-



Scheme 1. Synthesis of **4**.

methylester already shows similar solubility characteristics as Hostinert 216<sup>®</sup>: While adding the HFPO<sub>3</sub>-acidic fluoride to methanol, it forms a second layer.

The HFPO<sub>*n*</sub>-methylesters are then converted with an excess of acetone in a typical Claisen condensation [20] to the HFPO<sub>*n*</sub>-acac compound **3**. The structure of the obtained ligand was confirmed by <sup>1</sup>H NMR, <sup>19</sup>F NMR and IR spectroscopy.

The Ni-catalyst system **4** was formed in situ from **3** and [Ni(COD)<sub>2</sub>] either in toluene or in a biphasic system toluene/Hostinert. In the latter case the decolouration of the toluene layer was observed after a few minutes and the beforehand colourless Hostinert layer becomes yellow-brown.

### 3. Catalytic results and discussion

The catalytic results obtained with **4** are shown in Table 2. For case (a) and (b) the compound **4** was prepared in a biphasic system of toluene and Hostinert. In case (a) the Hostinert layer was separated and used as catalyst and in case (b) the toluene layer of the same experiment was used as catalyst. Unfortunately, the catalytic test reactions with these systems are not easy to interpret quantitatively because it was not possible to determine the exact content of active Ni catalyst in each phase. So the TON in Table 2 is calculated for the fictive case that all of the previously added catalyst would be active in the named reaction solvent. In this way the TON in Table 2 is the lowest possible

estimation for the real activity of the catalyst in the system.

Apart from the interpretation problems of the catalyst activity it was possible to observe two main differences between the reactions in cases (a) and (b). First, one can see that the products in case (a) form a second layer over the Hostinert, while the system in toluene (case b) remains a one-phase system. Second, the formed oligomer's maximum chain length is shorter in the Hostinert system. This is probably due to the lower ethylene solubility in Hostinert vs. the already formed product layer, which makes β-elimination more probable than a further ethylene insertion.

In experiments (c) and (d) the catalyst **4** was preformed in toluene. In case (c) one part of the toluene solution was directly used as catalyst. It is noteworthy that even in this case it was possible to add Hostinert after reaction to obtain a biphasic system. A nearly colourless upper layer contains product and toluene, while the Ni catalyst seemed to stay almost quantitatively in the lower phase. In case (d), Hostinert was added before reaction to form a biphasic system during reaction. Again, one could observe shorter maximum chain length of the products indicating that at least one part of the Ni catalyst is active in Hostinert.

### 4. Conclusion

Our catalytical experiments with **4** in Hostinert could demonstrate for the first time that the immobilisation of homogeneous transition metal

Table 2  
Catalytic results for the ethene oligomerisation with **4**

Solvent for catalyst formation	Solvent	Conversion	TON	Max. chain length
(a) Toluene/Hostinert	Hostinert	1.0		C16
(b) Toluene/Hostinert	Toluene	1.1		C22
(c) Toluene	Toluene	66.3	1890	C30
(d) Toluene	Toluene/Hostinert	73.4	2460	C24

Conditions: *p* = 50 bar; *T* = 90°C, *t* = 2 h; Ni catalyst:ethene = 1:3000.

catalysts in perfluorinated solvents is possible if an adapted ligand design is used. Unfortunately, no complete separation of catalyst phase and product phase could be obtained, but nevertheless the results show the usefulness of fluorinated solvents.

## References

- [1] Shell Oil, W. Keim, T.M. Shryne, R.S. Bauer, H. Chung, P.W. Glockner, H. van Zwet, U.S. Patent, (1968).
- [2] W. Keim, Chem. Ing. Tech. 56 (1984) 850.
- [3] E.G. Kuntz, CHEMTECH 17 (1987) 570.
- [4] B. Cornils, Chem. Ing. Tech. 66 (1990) 916.
- [5] B. Cornils, W.A. Herrmann, Homogeneous Catalysis with Organometallic Compounds, Vol. 2, Wiley-VCH, Weinheim, 1996, p. 832.
- [6] T. Prinz, W. Keim, B. Drießen-Hölscher, Angew. Chem. 108 (1996) 1835.
- [7] I.T. Horváth, J. Rábai, Science 266 (1994) 72.
- [8] J.J.J. Juliette, I.T. Horváth, J.A. Gladysz, Angew. Chem. 109 (1997) 1682.
- [9] G. Pozzi, F. Montanari, S. Quici, Chem. Commun. (1997) 69.
- [10] I. Klement, H. Lütjens, P. Knochel, Angew. Chem. 109 (1997) 1605.
- [11] J.-M. Vincent, A. Rabion, V.K. Yachandra, R.H. Fish, Angew. Chem. 109 (1997) 2438.
- [12] M. Vogt, dissertation, RWTH Aachen, 1991.
- [13] B. Cornils, Angew. Chem. 107 (1995) 1709.
- [14] B. Cornils, Angew. Chem. 109 (1997) 2147.
- [15] R. Lodewick, dissertation, RWTH Aachen, 1977.
- [16] W. Keim, B. Hoffmann, R. Lodewick, M. Peukert, G. Schmitt, J. Fleischhauer, U. Meier, J. Mol. Catal. 6 (1979) 79.
- [17] S. Gruppe, dissertation, RWTH Aachen, 1988.
- [18] A. Mehlhorn, dissertation, RWTH Aachen, 1991.
- [19] H. Millauer, W. Schwertfeger, G. Siegmund, Angew. Chem. 97 (1985) 164.
- [20] A.E. Pedler, R.C. Smith, J.C. Tatlow, J. Fluorine Chem. 1 (1977) 433.